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**Stratospheric Tracers of Atmospheric Transport
(STRAT) Campaign: ER-2 Participation**

Final Technical Report

NASA Agreement NCC-2-913 ↓
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A Final Report: STRAT Campaign: ER-2 Participation (NASA Cooperative Agreement NCC 2-892)

The NASA Stratospheric Tracers of Atmospheric Transport (STRAT) mission was initiated to advance knowledge of the major transport mechanisms of the upper troposphere-lower stratosphere. This is the region of the atmosphere within which exchange processes take place that critically determine the response of the climate system and ozone distribution to changing conditions triggered by the release of chemicals at the surface. The mission series that extended from October 1995 to November 1997 was extremely successful. The scientific advances that emerged from that mission include analyses of:

- troposphere-to-stratosphere transport in the lowermost stratosphere from measurements of H_2O , CO_2 , N_2O , and O_3 ;
- the effects of tropical cirrus clouds on the abundance of lower stratospheric ozone;
- the role of HO_x in super- and subsonic aircraft exhaust plumes; and
- dehydration and denitrification in the arctic polar vortex during the 1995-96 winter.

The abstracts from published results of this mission are presented here in the order that they appeared in the literature.

1. Dessler, A. E., K. Minschwaner, E. M. Weinstock, E. J. Hints, and J. G. Anderson, "The effects of tropical cirrus clouds on the abundance of lower stratospheric ozone," *J. Atmos. Chem.* **23**, 209-220, 1996. The distribution of many chemical constituents of the atmosphere (e.g., ozone) is at least partially determined by the distribution of net radiative heating in the atmosphere. In this paper, we demonstrate the significant effect of high cirrus clouds on the net radiative heating of the tropical lower stratosphere. A model of tropical lower stratospheric ozone is then used to demonstrate the sensitivity of calculated ozone to the varying cloud cover used in the model. We conclude that calculated ozone is sensitive to the inclusion of clouds in models and that models of the atmosphere should include a realistic description of the tropical cirrus clouds in order to accurately simulate the chemical composition of the atmosphere.
2. Hanisco, T. F., P. O. Wennberg, R. C. Cohen, J. G. Anderson, D. W. Fahey, E. R. Keim, R. S. Gao, R. C. Wamsley, S. G. Donnelly, L. A. Del Negro, R. J. Salawitch, K. K. Kelly, and M. H. Proffitt, "The role of HO_x in super- and subsonic aircraft exhaust plumes," *Geophys. Res. Lett.* **24**, 65-68, 1997. The generation of sulfuric acid aerosols in aircraft exhaust has emerged as a critical issue in determining the impact of supersonic aircraft on stratospheric ozone. It has long been held that the first step in the mechanism of aerosol formation is the oxidation of SO_2 emitted from the engine by OH in the exhaust plume. We report here *in situ* measurements of OH and HO_2 in the exhaust plumes of a supersonic (Air France Concorde) and a subsonic (NASA ER-2) aircraft in the lower stratosphere. These measurements imply that reactions with OH are responsible for oxidizing only a small fraction of SO_2 (2%), and thus cannot explain the large number of particles observed in the exhaust wake of the Concorde.
3. Wennberg, P. O., T. F. Hanisco, L. Jaeglé, D. J. Jacob, E. J. Hints, E. J. Lanzendorf, J. G. Anderson, R. S. Gao, E. R. Keim, S. G. Donnelly, L. Del Negro, D. W. Fahey,

- S. A. McKeen, R. J. Salawitch, C. R. Webster, R. D. May, R. L. Herman, M. H. Proffitt, J. J. Margitan, E. L. Atlas, C. T. McElroy, J. C. Wilson, C. A. Brock, and T. V. Bui, "Hydrogen radicals, nitrogen radicals, and the production of ozone in the middle and upper troposphere," *Science* **279**, 49–53, 1998. The concentrations of the hydrogen radicals OH and HO₂ in the middle and upper troposphere were measured simultaneously with those of NO, O₃, CO, H₂O, CH₄, non-methane hydrocarbons, and with the ultraviolet and visible radiation field. The data allow a direct examination of the processes that produce O₃ in this region of the atmosphere. Comparison of the measured concentrations of OH and HO₂ with calculations based on their production from water vapor, ozone, and methane demonstrate that these sources are insufficient to explain the observed radical concentrations in the upper troposphere. The photolysis of carbonyl and peroxide compounds transported to this region from the lower troposphere may provide the source of HO_x required to sustain the measured abundances of these radical species. The mechanism by which NO affects the production of O₃ is also illustrated by the measurements. In the upper tropospheric air masses sampled, the production rate for ozone (determined from the measured concentrations of HO₂ and NO) is calculated to be about 1 part per billion by volume each day. This production rate is faster than previously thought and implies that anthropogenic activities that add NO to the upper troposphere, such as biomass burning and aviation, will lead to production of more O₃ than expected.
4. Hints, E. J., P. A. Newman, H. H. Jonsson, C. R. Webster, R. D. May, R. L. Herman, L. R. Lait, M. R. Schoeberl, J. W. Elkins, P. R. Wamsley, G. S. Dutton, T. P. Bui, D. W. Kohn, and J. G. Anderson, "Dehydration and denitrification in the arctic polar vortex during the 1995–96 winter," *Geophys. Res. Lett.* **25**, 501–504 1998. Dehydration of more than 0.5 ppmv water was observed between 18 and 19 km ($\theta \sim 450$ –465 K) at the edge of the arctic polar vortex on February 1, 1996. More than half the reactive nitrogen (NO_y) had also been removed, with layers of enhanced NO_y at lower altitudes. Back trajectory calculations show that air parcels sampled inside the vortex had experienced temperatures as low as 188 K within the previous 12 days, consistent with a small amount of dehydration. The depth of the dehydrated layer (~ 1 km) and the fact that trajectories passed through the region of ice saturation in one day imply selective growth of a small fraction of particles to sizes large enough (> 10 μm) to be irreversibly removed on this timescale. Over 25% of the arctic vortex in a 20–30 K range of θ is estimated to have been dehydrated in this event.
 5. Hints, E. J., K. A. Boering, E. M. Weinstock, J. G. Anderson, B. L. Gary, L. Pfister, B. C. Daube, S. C. Wofsy, M. Loewenstein, J. R. Podolske, J. J. Margitan and T. P. Bui, "Troposphere-to-stratosphere transport in the lowermost stratosphere from measurements of H₂O, CO₂, N₂O and O₃," *Geophys. Res. Lett.* **25**, 2655–2658, 1998. The origin of air in the lowermost stratosphere is investigated with measurements from the NASA ER-2 aircraft. Air with high water vapor mixing ratios was observed in the stratosphere at $\theta \sim 330$ –380 K near 40 N in May 1995, indicating the influence of intrusions of tropospheric air. Assuming that observed tracer-tracer relationships reflect mixing lines between tropospheric and stratospheric air masses, we calculate mixing ratios of H₂O (12–24 ppmv) and CO₂ for the admixed tropospheric air at $\theta = 352$ –364 K. Temperatures on the 355 K surface at 20–40 N

were low enough to dehydrate air to these values. While most ER-2 CO₂ data in both hemispheres are consistent with tropical or subtropical air entering the lowermost stratosphere, measurements from May 1995 for $\theta < 362$ K suggest that entry of air from the midlatitude upper troposphere can occur in conjunction with mixing processes near the tropopause.

6. Stimpfle, R. M., R. C. Cohen, G. P. Bonne, P. B. Voss, K. K. Perkins, L. C. Koch, J. G. Anderson, R. J. Salawitch, S. A. Lloyd, R. S. Gao, L. A. Del Negro, E. R. Keim, and T. P. Bui, "The coupling of ClONO₂, ClO and NO₂ in the lower stratosphere from *in situ* observations using the NASA ER-2 aircraft," *J. Geophys. Res.*, submitted December 1998. The first *in situ* measurements of ClONO₂ in the lower stratosphere, acquired using the NASA ER-2 aircraft during the Polar Ozone Loss in the Arctic Region in Summer (POLARIS) mission, are combined with simultaneous measurements of ClO, NO₂, temperature, pressure, and the calculated photolysis rate coefficient (J_{ClONO_2}) to examine the balance between production and loss of ClONO₂. The observations demonstrate that the ClONO₂ photochemical steady state approximation, $[\text{ClONO}_2]^{\text{PSS}} = k \times [\text{ClO}] \times [\text{NO}_2] / J_{\text{ClONO}_2}$, is in good agreement with the direct measurement, $[\text{ClONO}_2]^{\text{MEAS}}$. For the bulk of the data (80%), where $T > 220$ K and latitudes $> 45^\circ\text{N}$, $[\text{ClONO}_2]^{\text{PSS}} = 1.15 \pm 0.36 (1\sigma) \times [\text{ClONO}_2]^{\text{MEAS}}$, while for $T < 220$ K and latitudes $< 45^\circ\text{N}$ the result is somewhat less at 1.01 ± 0.30 . The cause of the temperature and/or latitude trend is unidentified. These results are independent of solar zenith angle and air density, thus there is no evidence in support of a pressure-dependent quantum yield for photodissociation of ClONO₂ at wavelengths > 300 nm. These measurements confirm the mechanism by which active nitrogen ($\text{NO}_x = \text{NO} + \text{NO}_2$) controls the abundance of active chlorine ($\text{Cl}_x = \text{ClO} + \text{Cl}$) in the stratosphere.

The field deployment grant was extended, subsequently, to include the Photochemistry of Ozone Loss in the Arctic Region in Summer (POLARIS). That mission was flown between April 1997 and October 1997. Abstracts are presented for the following papers, which have been submitted for publication in a special issue of *Journal of Geophysical Research—Atmospheres*, scheduled for publication in Fall 1999:

1. Lazendorf, E. J., T. F. Hanisco, R. M. Stimpfle, J. G. Anderson, P. O. Wennberg, R. L. Herman, R. C. Cohen, D. W. Fahey, R. S. Gao, C. R. Webster, R. D. May, J. J. Margitan, and T. P. Bui, "Establishing the dependence of $[\text{HO}_2]$ on temperature, halogen loading, ozone, and NO_x ," *J. Geophys. Res.*, submitted 1999. A large database of measurements from the last three NASA ER-2 field campaigns is used to examine HO_x ($\text{HO} + \text{HO}_2$) photochemistry in the lower stratosphere and upper troposphere. These measurements cover a latitude range of 70°S to 90°N and a wide variety of atmospheric conditions. *In situ* measurements of the chemical species important in HO_x partitioning are compared to laboratory-measured reaction rates by examining the ratio of HO_2/OH . HO_x partitioning is accurately described ($\pm 10\%$) by mechanisms that include the rate limiting steps for (1) direct and indirect removal of O_3 by HO_x in the lower stratosphere, and (2) the production of O_3 in the upper troposphere. Because $[\text{OH}]$ is roughly constant in the lower stratosphere, the ratio of HO_2/OH reflects the variability of $[\text{HO}_2]$ to the concentrations of other chemical species. The response of the HO_2/OH ratio shows how HO_x concentrations respond to

- photochemical changes. The effects of halogen loading, $[O_3]$, $[NO_x]$, and temperature, upon the HO_2/OH ratio are examined.
2. Perkins, K. K., T. F. Hanisco, R. C. Cohen, L. C. Koch, R. M. Stimpfle, P. B. Voss, G. P. Bonne, E. J. Lanzendorf, J. G. Anderson, P. O. Wennberg, R. -S. Gao, L. A. Del Negro, E. R. Keim, S. G. Donnelly, D. W. Fahey, and R. J. Salawitch, "An examination of the NO_2/HNO_3 ratio in the lower stratosphere during periods of continuous sunlight," *J. Geophys. Res.*, submitted 1999. During the 1997 Photochemistry of Ozone Loss in the Arctic Region in Summer (POLARIS) mission, simultaneous, *in situ* observations of the principal radical and reservoir species of the nitrogen, hydrogen, and halogen families were obtained in the high-latitude, lower stratosphere during summer. These observations are ideal for examining the steady-state partitioning between NO_2 and HNO_3 during periods of continuous sunlight where the exchange between NO_2 and $HONO_3$ is dominated by gas-phase processes. Calculations of NO_x production and loss show that when 1997 JPL rate coefficient recommendations are used, loss exceeds production by 53%, where a balance is expected. Using new laboratory measurements of the reaction rate coefficients for $OH + HNO_3$ and $OH + NO_2$ reduces this discrepancy to 11%. Combining this analysis with an analogous, but independent, analysis of the HO_x system indicates that the precision in estimating overhead O_3 from TOMS satellite measurements is sufficiently poor as to hamper analyses of both systems. The measurements also exhibit a strong, almost linear correlation between the photolysis rate of HNO_3 (J_{HNO_3}) and $[OH]$, which results in a remarkably constant partitioning between the two NO_x production processes with HNO_3 photolysis and reaction with OH , accounting for 59% and 41% of the production, respectively. Because of strong J_{HNO_3} - OH relationship, the steady-state $[NO_2]_{24hr-avg}/[HNO_3]$ ratio reduces to a simple function of temperature and $[M]$. Indeed, the *in situ* observations reveal a compact relationship between the $[NO_2]_{24hr-avg}/[HNO_3]$ ratio and $[M]$ over a range of latitude, $[O_3]$, $[NO_y]$, particle surface area, albedo, and overhead O_3 . Because of the simplicity of this functional relationship, the steady-state $[NO_2]_{24hr-avg}/[HNO_3]$ ratio can be easily and accurately predicted throughout the region of continuous sunlight.
 3. Hanisco, T. F., E. J. Lanzendorf, R. M. Stimpfle, G. P. Bonne, E. J. Hintsa, K. K. Perkins, R. M. Stimpfle, P. B. Voss, J. G. Anderson, P. O. Wennberg, R. Herman, R. C. Cohen, L. C. Koch, D. W. Fahey, R. -S. Gao, E. R. Keim, S. G. Donnelly, L. A. Del Negro, M. H. Proffitt, R. J. Salawitch, C. R. Webster, R. D. May, S. A. Lloyd, T. McElroy, C. Midwinter, and P. Bui, "Sources, sinks, and the distribution of OH in the lower stratosphere," *J. Geophys. Res.*, submitted 1999. Extensive measurement campaigns by the NASA ER-2 have obtained a pole-to-pole database of the species that control HO_x ($OH + HO_2$) chemistry. The wide dynamic range of these *in situ* measurements provides an opportunity to gain insight into the mechanisms that control the HO_x system. Measurements in the lower stratosphere show a remarkably tight correlation of OH concentration with Solar Zenith Angle (SZA), which is invariant over latitudes ranging from $70^\circ S$ to $90^\circ N$ and all seasons. Calculations using *in situ* measurements show that the production rate of OH is proportional to O_3 and ultraviolet radiation flux and the loss rate is proportional to the concentration of NO_y (reactive nitrogen). Since O_3 and NO_y are correlated, the concentration of OH is fairly

constant within this data set. Changes in the partitioning within NO_x have a dramatic effect on the loss rates of HO_x , but little or no impact on the measured abundance of OH. The heterogeneous conversion of NO_2 to HNO_3 is not a net source of HO_x because production and removal cycles are nearly balanced. Furthermore, the enhanced loss rates at high NO_2/HNO_3 are offset by increased photolysis rates resulting from decreased O_3 column above the ER-2.

4. Bonne, G. P., R. M. Stimpfle, R. C. Cohen, P. B. Voss, K. K. Perkins, J. G. Anderson, C. R. Webster, D. C. Scott, R. D. May, R. J. Salawitch, J. W. Elkins, R. E. Dunn, G. S. Dutton, K. W. Jucks, G. C. Toon, and B. Sen, "An examination of the inorganic chlorine budget in the lower stratosphere," *J. Geophys. Res.*, submitted 1999. We use the first simultaneous *in situ* measurements of ClONO_2 , ClO , and HCl acquired using the NASA ER-2 aircraft during the Photochemistry of Ozone Loss in the Arctic Region in Summer (POLARIS) mission to test whether these three compounds quantitatively account for total inorganic chlorine (Cl_y) in the lower stratosphere in 1997. We find $(\text{ClO} + \text{ClONO}_2 + \text{HCl})/\text{Cl}_y = 0.92 \pm 0.10$, where Cl_y is inferred from *in situ* measurements of organic chlorine source gases. These observations are consistent with our current understanding of the budget and partitioning of Cl_y in the lower stratosphere. We find no evidence in support of missing inorganic chlorine species that comprise a significant fraction of Cl_y . We apply the analysis to earlier ER-2 observations dating from 1991 to investigate possible causes of previously observed discrepancies in the inorganic chlorine budget. Using space shuttle, satellite, balloon and aircraft measurements in combination with ER-2 data we find that the discrepancy is unlikely to have been caused by missing chlorine species or an error in the photolysis rate of chlorine nitrate. We also find HCl/Cl_y is not significantly controlled solely by aerosol surface area density in the lower stratosphere.
5. Bonne, G. P., R. M. Stimpfle, R. C. Cohen, P. B. Voss, K. K. Perkins, L. C. Koch, E. J. Hintsa, S. A. Lloyd, and J. G. Anderson, "*In situ* measurements of ClONO_2 : A new thermal dissociation resonance fluorescence instrument on board the NASA ER-2 aircraft," *J. Geophys. Res.*, submitted 1999. A new instrument for the *in situ* measurement of ClONO_2 density in the lower stratosphere from the NASA ER-2 aircraft is described. The technique of thermal dissociation of ClONO_2 is coupled with the proven chemical conversion/atomic resonance scattering technique for measurement of ClO . The sampled ambient air stream is heated to 520 K, thermally dissociating ClONO_2 to ClO and NO_2 within 5 msec. The ClO fragment is reacted with added NO to form Cl atoms, which are detected using atomic resonance fluorescence at 118.9 nm. Laboratory calibrations and aircraft measurements demonstrate that the technique can be described by gas phase processes. ClONO_2 is detected with an accuracy of 20% (1σ) and a detection threshold of 10 parts per trillion in a 35-second integration time. The instrument has provided the first *in situ* measurements of ClONO_2 during the Photochemistry of Ozone Loss in the Arctic Region in Summer (POLARIS) mission staged out of Fairbanks, AK in 1997. These measurements, taken with other simultaneous measurements from the ER-2, provide the means for a detailed examination of the budget and partitioning of inorganic chlorine and the production and loss of ClONO_2 in the lower stratosphere.

6. Voss, P. B., R. M. Stimpfle, T. F. Hanisco, G. P. Bonne, K. K. Perkins, E. J. Lanzendorf, J. G. Anderson, R. C. Cohen, L. C. Koch, C. R. Webster, D. C. Scott, R. D. May, R. J. Salawitch, J. J. Margitan, P. O. Wennberg, R. -S. Gao, T. P. Bui, P. A. Newman, and L. R. Lait, "Chlorine partitioning in the summer lower stratosphere: A comparison of modeled and measured chlorine partitioning during POLARIS," *J. Geophys. Res.*, submitted 1999. The first *in situ* measurements of ClONO₂ (made during the POLARIS campaign in the summer of 1997) are used in conjunction with calculated photolysis rates and measurements of HCl, O₃, CH₄, NO, NO₂, and OH to examine the processes that control gas-phase partitioning of Cl_y in the lower stratosphere. Diurnal steady-state and trajectory models of gas-phase chlorine chemistry (constrained by measured OH and NO_x) demonstrate that the rate constants and photolysis cross-sections of JPL97 overpredict [ClONO₂]/[HCl] by 45–60% in comparison with measurements. This error is significantly greater than reported in previous studies that mask errors in Cl_y partitioning by using modeled OH. A treatment of ratio statistics quantifies model-measurement dispersion; for the ratio [ClONO₂]/[HCl], dispersion is reduced significantly when photolysis rates are based on average climatology instead of local conditions. A framework for this analysis is provided by averaging a steady-state approximation for [ClONO₂]/[HCl] and factoring it into chemical, photolytic, and meteorological terms. This separation elucidates the effects of latitude, season, and altitude on Cl_y partitioning. A method for estimating time constants is developed and used to demonstrate that [ClONO₂]/[HCl] reaches steady-state with an *e*-folding time of approximately 2–10 days.
7. Smith, J. B., E. J. Hints, and J. G. Anderson, "Mechanisms for midlatitude ozone loss: Cirrus clouds in the stratosphere?" *J. Geophys. Res.*, submitted 1999. The question of midlatitude ozone erosion by chlorine free radical catalytic destruction is examined. Simultaneous, high-resolution observations of ClO, H₂O, tropopause position, particle reactive surface area, and ice saturation occurrence frequency obtained from the NASA ER-2 are presented. The objective is to test the hypothesis that the existence of cirrus clouds or cold aerosols in the first few kilometers above the tropopause at midlatitudes is responsible for increasing the ratio of chlorine free radicals to total inorganic chlorine and thus amplifying the rate of catalytic ozone destruction. The observations reveal a sharp decrease in cloud occurrence frequency immediately above the tropopause, a marked degree of undersaturation immediately above the tropopause, a corresponding sharp gradient in the product of cold aerosol reactive surface area and reaction probability, γS_a , and, finally, the consistent absence of enhanced concentrations of ClO immediately above the tropopause. These results suggest that midlatitude ozone erosion is not controlled *in situ* by the mechanism of cirrus cloud and/or cold aerosol enhancement of chlorine radicals in the vicinity of the tropopause.